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PATENT SPECIFICATION (11) 1234641

(54) NOBLE METAL CATALYSTS AND CATALYTIC PROCESSES

(71) We, MONSANTO COMPANY, a corporation organised under the laws of the State of Delaware, United States of America, of 800, North Lindbergh Boulevard, St. Louis 66, State of Missouri, United States of America, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement: —

This invention relates to catalysts and processes of using them.

According to the present invention there is provided a process for the treatment of a reactant which is an alkyl compound having n carbon atoms, where n is a number from 1 to 20, or an aryl compounds having n carbon atoms, where n is a whole number from 6 to 20, the said reactant being an alcohol, halide, ester, ether or phenol, to obtain a mixture comprising an organic acid having n+1 carbon atoms, or an ester of the alcohol having n carbon atoms with the said acid, which process comprises reacting the said reactant at a temperature of at least 50°C, with carbon monoxide in the presence as catalyst of a noble metal component selected from iridium, platinum, palladium, osmium and ruthenium and their compounds, and a promoter substance which is a halogen or halogen compound. The promoter substance is preferably selected from bromine, iodine, and compounds of bromine and of iodine.

This invention relates particularly to a process for the reaction of alcohols and carbon monoxide in the presence of catalyst compositions essentially comprising iridium, platinum, palladium, osmium, and ruthenium or their compounds or complexes, to yield carboxylic acids and esters selectively and efficiently.

In the following description and in the claims the term "noble metal" is used to mean only iridium, platinum, palladium, osmium, and ruthenium.

Carbonylation process for the preparation of carboxylic acids from alcohols are well known in the art and have been directed especially to the production of acetic acid by the carbonylation of methanol. The prior art teaches the use of a number of catalysts for the synthesis of carboxylic acids by reaction of alcohols with carbon monoxide at elevated temperatures and pressures in both gas phase fixed bed reactions and liquid phase reactions. Catalysts such as phosphoric acid, phosphates, activated carbon, heavy metal salts such as zinc and cuprous chlorides, silicates of various metals, and boron trifluoride in various hydration states have been reported to function for the production of acetic acid by reaction of methyl alcohol and carbon monoxide at elevated temperatures and pressures of the order of 400°C and 10,000 psig, respectively. However, even under such severe conditions the yields of acid were substantially poor, and, therefore, uneconomical. Somewhat less severe reaction conditions of temperature and/or pressure have been reported in the literature employing specific catalyst compositions, e.g., 330°C—340°C and 2250 psig using liquid phosphoric acid containing copper phosphate; 300°C—500°C and 2000 psig—4000 psig using active charcoal impregnated with phosphoric acid; and 260°C—360°C and 2800 psig—15,000 psig using metal carbonyls, such as iron, cobalt and nickel, in conjunction with their halides or free halogens in the liquid phase. Even using these specific catalyst compositions at the less severe reaction conditions, substantially poorer yields of the desired carboxylic acid product and substantially slower reaction rates are obtained than those achieved in the process of this invention.

Certain disadvantages present in the

carbonylation processes described in the prior art are catalyst instability, lack of product selectivity, and low levels of catalyst reactivity. One particular disadvantage of carbonylation processes of the prior art is their dependence upon the use of catalysts comprised of metal carbonyls or certain modified metal carbonyls including dicobalt octacarbonyl, iron carbonyl and nickel carbonyl, all of which require the use of high partial pressures of carbon monoxide to remain stable under the necessarily high reaction temperatures employed. For example, dicobalt octacarbonyl requires partial pressures of carbon monoxide as high as 3000 psig to 10,000 psig under normal carbonylation conditions of 175°C to 300°C.

Still another disadvantage of carbonylation processes disclosed in the prior art is their relatively low level of activity. This low level of activity requires higher catalyst concentrations, longer reaction times, and higher temperatures to obtain substantial reaction rates and conversions. Consequently larger and costlier processing equipment is required.

Another disadvantage of carbonylation processes disclosed heretofore is their inability to maintain high selectivity to the desired carboxylic acid at temperatures required for high conversion levels and high reaction rates. At these higher temperatures undesirable byproducts comprising substantial amounts of ethers, aldehydes, higher carboxylic acids, carbon dioxide, methane and water are formed, thereby resulting in substantial yield losses and necessitating additional product purification and recycle steps in the processing.

Another disadvantage of carbonylation processes described in the prior art is their dependence on catalyst systems which require the use of substantially chemically pure carbon monoxide feedstocks to maintain high selectivity and high yield to the desired carboxylic acid product. For example, certain cobalt containing catalyst systems described heretofore when employed with carbon monoxide feed streams containing impurities such as hydrogen, result in the production of a number of undesirable byproducts including methane, carbon dioxide, aldehydes, alcohols of the same carbon number as the desired carboxylic acid, and carboxylic acids of higher carbon number than desired. Consequently, substantial loss in selectivity and yield to the desired carboxylic acid occurs. Catalysts of the prior art cause the formation of troublesome gaseous byproducts such as carbon dioxide and methane as well as dimethyl ether in the reactor system, thereby suppressing the carbon monoxide partial pressure and ultimately causing a decrease in the desired carbonylation reaction rate. Often additional processing steps are required to remove these undesirable byproducts, necessitating the use of larger and costlier processing equipment.

It is, therefore, an object of the present invention to overcome the above disadvantages and thus provide an improved and more economically and commercially feasible carbonylation process for the production of organic acids and their esters.

Another object of this invention is to provide a more reactive and more stable carbonylation catalyst composition than has been heretofore described in the prior art.

Still another object of the present invention is to provide a more selective and more reactive carbonylation catalyst composition for the production of carboxylic acids.

Still another object of the present invention is the provision of an improved carbonylation process enabling the efficient and selective production of carboxylic acids or their esters by reaction of alcohols and alcohol derivatives with carbon monoxide in the presence of an improved and more stable catalyst, thus enabling the use of lower catalyst concentration, lower temperature, lower pressure, and shorter contact time than has been generally possible heretofore and facilitating product isolation, catalyst recovery and recycle without substantial catalyst decomposition and loss.

These and other objects of the present invention will become apparent to those skilled in the art from the accompanying description and disclosure of the vapor phase and liquid phase embodiments of the invention.

In the vapor phase embodiment of the invention, alcohols having n carbon atoms are converted selectively to a mixture comprised of an acid having n+1 carbon atoms and the ester of the said alcohol with the said acid, by reacting the alcohol or an alcohol derivative in the vapor phase with carbon monoxide at temperatures from 50°C to 500°C and at partial pressures of carbon monoxide from 0.1 psia to 15,000 psia, preferably 5 psia to 3,000 psia, and more preferably 10 psia to 700 psia, although higher pressure may be employed, in the presence of a catalyst system essentially comprised of the above noble metal component, and a halogen promoter. These may be dispersed upon a carrier. The carrier or substrate which may be employed in the present catalysts may consist of a porous solid of such size that it can be employed in fixed or fluidized-bed reactors, e.g., from 400 mesh/inch to 1/2-inch particle sizes. The range of variation of the pore volume relative to solid weight is from 0.03 to 2.5 cm³/gm of the porous phase; preferred range 0.05 to 1.5 cm³/gm.

The carrier materials are exemplified, but not limited by pumice, alumina, silica, silica-alumina, aged or deactivated silica-alumina cracking catalyst, magnesia, diatomaceous earth, bauxite, titania, zirconia, clays, both natural and acid treated such as the Super-Filtrols, attapulgus clay (attapulgite), lime, magnesium silicate, silicon carbide, activated and unactivated carbons, zeolites as well as the zeolitic molecular sieves, solid foams, such as

ceramic honeycombs, and porous organic polymers. The above carriers are used as regular and irregular particles and as capillary tubes, and interspacing elements such as shapes, extrudates, ceramic rods, balls, broken pieces, and tiles, disposed within the reactor.

In accordance with the present invention, alcohols having n carbon atoms are converted selectively to a mixture comprised of an acid having n+1 carbon atoms and the ester of the said alcohol with the said acid, by reacting the alcohol or an alcohol derivative in the liquid phase with carbon monoxide at temperatures from about 50°C to 300°C and at partial pressures of carbon monoxide from 1 psig to 15,000 psig preferably 5 psig to 3,000 psig, and more preferably 10 psig to 1000 psig, although higher pressure may be employed, in the presence of a catalyst system comprised of an active portion, viz an iridium, platinum, palladium, osmium or ruthenium, preferably an iridium containing component, and a promoter portion, which is, a halogen and/or halogen compound, preferably bromine or iodine. The present process is particularly advantageous at lower pressures, although higher pressures may also be used.

The catalyst contains as a major element thereof, a source providing an iridium, platinum, palladium, osmium or ruthenium component. For example, as referred to above,

for purposes of the present invention, the catalyst as charged is a noble metal compound containing the metal, halogen, and other moieties if desired. The catalyst essentially includes a noble metal component, as the active component, such as $IrCl_3$, $PbBr_3$, $Pt(CO)_4Br_2$,

$$OsCl_3(CO)[(n-C_4H_9)_3P]_2 \text{ and }$$

$$Ru(Cl)_2(CO)[(C_6H_5)_3P]_3.$$
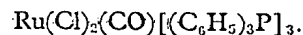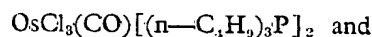
However, the catalyst is composed of two distinct components, namely the active catalyst portion, e.g., the aforesaid noble metal compound, as the first component, and a promoting portion as the second component which may or may not be catalytically active, but which aids the reaction in various ways, such as by facilitating cleavage of the carbon-oxygen bond in the alcohol.

The active catalytic portion or first component is palladium, platinum, iridium, osmium or ruthenium metal, simple palladium, platinum, iridium, osmium and ruthenium oxides and salts, organopalladium, organoplatinum, organoiridium, organoosmium and organoruthenium compounds, and coordination compounds of palladium, platinum, iridium, osmium and ruthenium, specific examples of which may be taken from the partial lists of suitable compounds below.

$IrCl_3$	Ir Metal, Ir_2O_3, $Ir(NO_3)_3$.
$IrBr_3$	$[(n-C_4H_9)_4N]$ $[Ir(CO)_3X_2]$ where X = Cl, Br, I.
IrI_3	$[(n-C_4H_9)_4As]_2[Ir_2(CO)_2Y_4]$ where Y = Br, I.
$IrCl_3.3H_2O$	$[(n-C_4H_9)_4P]$ $[Ir(CO)I_4]$
$IrBr_3.3H_2O$	Ir $[(C_6H_5)_3P]_2$ $(CO)Br$
$Ir_2(CO)_4Cl_2$	Ir $[(n-C_4H_9)_3P]_2(CO)Br$
$Ir_2(CO)_4Br_2$	Ir $[(n-C_4H_9)_3P]_2(CO)I$
$Ir_2(CO)_4I_2$	$IrBr$ $[(C_6H_5)_3P]_3$
$Ir_2(CO)_8$	IrI $[(C_6H_5)_3P]_3$
Ir $[(C_6H_5)_3P]_2(CO)I$	$IrCl[(C_6H_5)_3P]_3$
Ir $[(C_6H_5)_3P]_2(CO)Cl$	$IrCl[(C_6H_5)_3P]_3H_2$
$IrCl$ $[(C_6H_5)_3P]_2$ $(CH_3I)_2$	$[(C_6H_5)P]_3Ir(CO)H$
$Ir(SnCl_3)$ $[(C_6H_5)_3P]_3$	$[Ir(C_2H_4)_2Cl]_2$
$IrCl(CO)$ $[(C_6H_5)_3As]_2$	$K_4Ir_2Cl_2(SnCl_3)_4$
$IrI(CO)$ $[(C_6H_5)_3Sb]_2$	$K_4Ir_2Br_2(SnBr_3)_4$
$[Pt(CO)I_2]_2$	$K_4Ir_2I_2(SnI_3)_4$

$[Pd(CO)Cl_2]_2$

$Pt(CO)_2Cl_4$

$Pd[(C_6H_5)_3P]_2I_2$

$Pt[(C_6H_5)_3As](CO)I_2$

$Pd[(C_6H_5)_3P]_2(CO)Br$

$Pt[(C_6H_5)_3As]_2Cl_2$

$Pd[(n-C_4H_9)_3P]_2I_2$

$Pt(CH_3)[P(C_2H_5)_3]_2I$

Pd Metal

Pt Metal

$Pd(NO_3)_2$

PtO_2

$RuCl_3$

$RuBr_3$

RuI_3

$Ru(CO)_2I_2$

$Ru_3(CO)_{12}$

$RuCl_2(CO)[(C_6H_5)_3P]_3$

$RuI_2(CO)[(C_6H_5)_3As]_3$

$RuBr_2(CO)[(n-C_4H_9)_3P]_3$

$RuBr_3(CO)[(C_6H_5)_3P]_2$

Ru_2O_3

OsO_2

OsO_4

$K_2[Ru_2(SnCl_3)_2]$

$Os(CO)_4X_2$ where X = Cl, Br, I

PdO and PtO

$[(n-C_4H_9)_4N][Pt(CO)X_3]$ where X = Cl, Br, I

$[(n-C_4H_9)_4As]_2[PtX_4]$ where X = Cl, Br, I

$[(n-C_4H_9)_4P]_2[PdX_4]$ where X = Cl, Br, I

$[(C_2H_5)_3P]_2PtCH_3I$

$[P(C_6H_5)_3]_2 Pt(SnBr_3)_2$

$[(C_6H_5)_3PCH_3]_2PtCl_2(SnCl_3)_2$

$Pd[(n-C_4H_9)_3P](CO)Cl_2$

$[(C_6H_5)_3P](CO)Cl_2Pd$

$[(C_6H_5)_3As]_2PtCl(SnCl_3)$

OsX_3 and OsX_4 where X = Cl, Br, I

$Os(CO)_5$ and $Os_3(CO)_{12}$

$OsCl_3(CO)[(n-C_4H_9)_3P]_2$

$OsBr_3[(C_6H_5)_3As]_3$

$OsBr_2[(C_6H_5)_3P]_3$

$OsI_2[(C_6H_5)_3P]_3$

Os Metal

Ru Metal

The active catalytic portion or primary component of the catalyst system is preferably a coordination compound of the said noble metal, carbon monoxide, and a halide such as chloride, bromide and iodide, as well as suitable amine, organophosphine, organoarsine, and/or organostibine ligands and, if desired, other ligands, e.g., halide such as chloride, iodide and bromide, and trihalostannate such as the corresponding chloride, bromide or iodide, necessary to satisfy the coordination number and oxidation number of the central metal atom and thus form a coordination compound or complex of the noble metal such as

$$Pd_2(CO)_2Br_4, \quad Ir[(C_6H_5)_3P]_2(CO)Cl, \quad \text{or}$$

$$[(C_6H_5)_3P]_3Ru(CO)Cl_2$$

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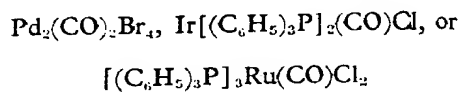
In the vapor phase embodiment it is possible that one or more of the ligand positions of the central metal atom is occupied by a group attached to the surface of the supporting structure such as carbon. The term coordination compound or coordination complex used throughout this specification means a compound or complex formed by combination of one or more electronically rich molecules or atoms capable of independent existence with one or more electronically poor molecules or atoms, each of which may also be capable of independent existence.

Suitable organo-nitrogen, organo-phosphorus, organo-arsenic, and organo-antimony ligands which may comprise part of the noble metal, i.e. iridium, platinum, palladium, osmium and ruthenium coordination compound or other catalyst are those consisting of tertiary organo-nitrogen, organo-phosphorus, organo-arsenic, and organo-antimony compounds in which the nitrogen, arsenic, phosphorus, and antimony atoms are trivalent and are referred to in this specification as amines, phosphines, arsines, and stibines, respectively. In the group of suitable ligands containing the trivalent nitrogen, phosphorus, arsenic, and antimony atoms employed in the catalyst of this invention, the individual nitrogen, phosphorus, arsenic, and antimony atom has one available or unshared pair of electrons. An organic derivative of trivalent nitrogen, phosphorus, arsenic, and antimony with the foregoing electronic configuration is, therefore, a suitable ligand for the noble metal containing catalyst of this invention. Organic radicals of any size and composition may be bonded to the nitrogen, phosphorus, arsenic, and antimony atoms, and the radicals are selected from the group consisting of alkyl and aryl groups. However, the preferred amine, phosphine, arsine, and stibine ligands are those consisting of at least one, but preferably one to three aryl-and/or aryloxy groups as the organic moieties. For example, preferred ligands are illustrated by the following structural formula and examples:

$$MR_3 \text{ where } M = N, P, As, Sb, \text{ and}$$

$$R = \text{phenyl } (C_6H_5\text{—}), \text{ phenoxy } (C_6H_5O\text{—}), \text{ tolyl } [CH_3(C_6H_5)\text{—}] \text{ n-butyl } (n\text{-}C_4H_9\text{—})$$

$$\text{e.g. } N(n\text{-}C_4H_9)_3, P(C_6H_5)_3, P(C_6H_5O)_3$$

$$As(C_6H_5)_3, Sb(C_6H_5)_3, P[CH_3(C_6H_5)]_3$$

A preferred group of ligands associated with the iridium and the other noble metal components, used with organic phosphorus, arsenic, and antimony derivatives has alkyl radicals of 1 to 18 carbon atoms, aryl radicals having from 6 to 18 carbon atoms and halogen radicals selected from the group consisting of chlorine, bromine and iodine. A preferred catalyst is composed of a noble metal atom, i.e. iridium, platinum, palladium, osmium and ruthenium, having as ligands, carbon monoxide, and at least one halogen ligand selected from the group consisting of chlorine, bromine and iodine, and at least two ligands selected from the group consisting of phosphorus, arsenic, and antimony derivatives having alkyl radicals of from 1 to 18 carbon atoms or aryl radicals having from 6 to 18 carbon atoms.

The promoting portion or second component of the catalyst system consists of a halogen and/or halogen compound such as hydrogen halide, alkyl- or aryl-halide, metal halide, ammonium, phosphonium, arsonium and stibonium halide, and may be the same or different from any halogen component already present in the active catalytic portion or first component of the catalyst system. Halogen or halide compounds are suitable for the promoter portion of the catalyst, but those containing iodine and bromine are preferred. Accordingly, suitable promoters comprising the second portion of the catalyst system may be selected from the following list of preferred halogen and/or halogen containing compounds:

RX   where   R = any alkyl- or   *e.g.* CH_3I, C_6H_5Br,

                        aryl-group CH_3CH_2I, etc.

            and   X = Cl, Br, or I

X_2 or X_3^- where   X = Cl, Br, or I, *e.g.*, Br_2, I_2, I_3^-

HX   where   X = Cl, Br, or I, *e.g.*, HBr, HI

$\underset{\underset{O}{\|}}{RCX}$ where   R = any alkyl- or *e.g.*, $\underset{\underset{O}{\|}}{CH_3CI}$,

                        aryl-group

            and   X = Cl, Br, or I

R_4MX, R_4MX_3, or R_3MX_2

            where R = Hydrogen or any alkyl- *e.g.*, NH_4I, PH_4I_3,

                  or aryl-group PH_3I_2, PH_3Br_2

            M = N, P, As, or Sb $(C_6H_5)_3PI_2$, and/or
                                         combinations of
            X = Cl, Br, or I   R, M, and X

The active catalyst or first component of the catalyst system may be preformed prior to charging the reactor, or it may be formed *in situ* on the carrier in the reactor. For example, it may consist of either palladium, platinum, iridium, osmium or ruthenium metals, a simple compound, carbonyl, carbonyl salt, or palladium, platinum, iridium, osmium and ruthenium in complex combination with carbon monoxide and suitable organo phosphine, arsine, or stibine ligands and also other ligands, e.g., halide as described above. Generally, and preformed palladium, platinum, iridium, osmium and ruthenium compound may be charged as a precursor to the reactor. If desired, the active catalytic noble metal component described above may be prepared from any of the simpler types of palladium, platinum, iridium, osmium and ruthenium salts.

The halogen promoter portion or second component of the catalyst may be charged to the reactor separately from the active catalyst or first component, or it may be incorporated into the active component, e.g., IrI_3. The active metal compound or first component of the catalyst system may be prepared prior to charging the reactor or generated *in situ*. Subsequently, after the first component is in the reactor either as a liquid phase catalyst solution or is dispersed upon a carrier, the promoter or second component of the catalyst may be added as a gaseous or liquid compound or as a solution in a suitable solvent. However, the promoter portion of the catalyst may also be incorporated in the active catalyst or first component during the *in situ* generation of the active catalyst. For example, to prepare the catalyst system, the first component of the catalyst system, e.g., finely divided metal (powder) or a simple salt or compound as discussed above is dissolved in a suitable medium, and in the vapor phase process is subsequently impregnated upon an inert support or carrier as discussed herein. Alternatively, to facilitate dissolution of the first component, carbon monoxide may be bubbled through the above catalyst solution, preferably while maintaining gentle heating and stirring of the said solution. Then an acidic solution of the desired halogen promoter may be added to form an active catalytic solution containing the necessary metal and halogen promoter components. This active catalytic solution may be used as a liquid phase catalyst or may be impregnated upon an inert support or carrier as discussed herein to generate the supported catalyst.

The solvent which is used to dissolve or disperse the metal catalytic component is a material having a low boiling point, e.g., high vapor pressure under reaction conditions. The range of variation of the boiling point (NBP, 760 mm Hg) is quite broad, a preferred range being from 10°C to 120°C.

It has been found that the preparation of a solid catalyst which is uniform in composition is preferably accomplished by the use of a volatile solvent component in the impregnation of an initially dry porous support with a catalytic component dissolved in the said solvents. The normal boiling point of the volatile liquid solvent is in the range of from 10°C

to 120°C. A preferable group of volatile solvents includes chloroform, carbon tetrachloride, benzene, acetone, methanol, ethanol, isopropanol, isobutanol, pentane, hexane, cyclohexane, heptane, toluene, pyridine, diethylamine, acetaldehyde, acetic acid, tetrahydrofuran and water.

The preparation of the solid phase catalyst is carried out by first dissolving or dispersing the metal moiety in the above described volatile solvent. The solid carrier is then impregnated with the solution of the metal moiety, for example, by pouring the solution upon the carrier, or immersing the solid carrier in an excess of the liquid solution, with the excess being subsequently removed.

The impregnated support or carrier is then maintained at a temperature sufficient to volatilize the solvent, preferably at a temperature between 15°C and 250°C, to permit drying of the composite solid catalyst. A vacuum may also be applied to the catalyst in order to volatilize the solvent, although the use of vacuum is not essential. During this stage of the process, the volatile solvent evaporates from the solid catalytic product. The final product is a solid supported catalyst.

For example, to prepare the catalyst system, the first component of the catalyst system, e.g., a palladium salt such as $PdCl_2$ is dissolved in a suitable solvent such as ethanol. Subsequently, carbon monoxide is bubbled through the solution where an intermediate, such as $Pd(CO)_2Cl_2$, is produced. This intermediate may be impregnated upon a carrier or, alternatively, the solution of the intermediate may have the promoter added to the solution. The second or promoter component may, for example, be added to the above solution, e.g., as aqueous HI, or methyl iodide or other iodine containing compound. This active catalyst solution may be used per se or the catalytic solution containing the necessary palladium and halide components for impregnation upon the carrier as discussed above. Often it may be beneficial and desirable to have the concentration of the second component or promoter portion of the catalyst system, for example, iodide such as HI or CH_3I, in excess of that required to form a stoichiometric compound such as described above. In the same way the two components, e.g., a palladium compound and an iodine or bromine component are provided in a single molecule by beginning with palladium iodide or palladium bromide as the catalyst for the reaction of an alcohol with carbon monoxide to produce an organic acid. The present discussion is based upon the catalyst precursors as charged. The ultimate nature of the catalyst as modified by reaction conditions, and the presence of promoters and reactants has not been completely elucidated. However, it has been found that the use of the components described herein provides a highly superior catalyst and process

for the production of acids.

Although any ratio of promoter portion or second component of the catalyst system may be employed, ratios of promoter portion to active portion expressed as atoms of halogen in the promoter portion to atoms of iridium in the active portion of the catalytic system in the range of 1:1 to 2500:1 are generally employed. However, the preferred range is 3:1 to 300:1 halogen atoms per noble metal, e.g., iridium atom.

The liquid reaction medium employed in the liquid phase process may be any solvent compatible with the catalyst system and may include pure alcohols, or mixtures of the alcohol feedstock and/or the desired carboxylic acid and/or esters of these two compounds. However, the preferred solvent and liquid reaction medium for the process of this invention is the desired carboxylic acid itself. Water may also be added to the reaction mixture to exert a beneficial effect upon the reaction rate. Other liquid phase reaction media may be chosen such as the organo-phosphorus ligands employed in preparation of the catalyst system. An example of such a ligand which may function as the liquid reaction medium and/or solvent is triphenylphosphite. Such a choice of ligand as solvent and/or reaction medium tends to improve catalyst stability and maintain catalyst selectivity, thereby substantially eliminating the need for providing another chemical compound to the liquid reaction medium.

Suitable feedstocks are alcohols although the alcohol may be charged together with ether, alkyl halide or ester as discussed below. Preferred alcohols have one carbon atom less than the desired carboxylic acid product. These feedstocks also include halide, ester, and other derivatives of the desired alcohol feedstock.

Polyhydric alcohols, cyclic ethers, and lactones may also be employed as starting materials for the production of polybasic acids, for example, catechol to yield ortho phthalic acid, or 1,4-butanediol to yield adipic acid, ethylene oxide to yield succinic acid. These feedstocks when subjected to reaction with carbon monoxide under the conditions described herein with the catalyst of the invention, yield polybasic acids or esters including lactones.

Examples of preferred feedstocks employed for the carbonylation reaction of the present invention include the group of aliphatic alcohols having 1 to 20 carbon atoms including methanol, ethanol, propanol and isopropanol, the butanols, pentanols, phenol and hexanols, and also the higher alcohols such as the decanols, including isomeric forms. However, an alcohol is the preferred feedstock. For example, if acetic acid is the desired product, the feedstock may consist of methyl alcohol, or derivatives thereof, such as dimethyl ether, methyl acetate, and/or combinations of these.

In accordance with the present invention the

carbonylation reaction may be carried out by intimately contacting an alcohol, which depending on the carbon number and operating conditions may either be in the vapor or liquid phase, with gaseous carbon monoxide in a liquid phase containing the catalyst system such as iodocarbonylbistriphenylphosphine iridium (I), optionally in the presence of additional triphenylphosphine and halogen-containing promoter, such as methyl iodide, under conditions of temperature and pressure suitable as described herein to form the carbonylation product. The particular conditions selected are the same whether the alcohol is charged as a vapor or liquid. The temperature accordingly will be in the range of 50°C to 300°C with the preferred range being 100°C to 240°C. Partial pressures of carbon monoxide of the order of 1 psig to 15,000 psig may be employed, however, 5 psig to 3000 psig carbon monoxide partial pressure is generally preferred and a more preferred range is from 10 psig to 1000 psig. Higher pressures may be used if desired under appropriate conditions.

Alternatively, carboxylic acids may be produced if desired via reaction of alcohols and carbon monoxide in the vapor phase over the noble metal, e.g., iridium, containing catalyst systems described above, dispersed upon inert supports. Such a catalyst system may be operated as a conventional fixed bed catalytic reactor. For example, methyl alcohol, methyl iodide, and carbon monoxide may be passed over a catalyst system consisting, for example, of $Ir(CO)Cl[(C_6H_5)_3P]_2$ dispersed on an inert support material such as alundum, activated carbon, clays, alumina, silica-alumina, and ceramics, in a fixed bed reactor maintained at elevated temperature and pressure, as described above, to produce acetic acid in high yields. However, use of a liquid reaction medium is preferred in the process of this invention using dissolved or dispersed active catalytic and promoter components.

In accordance with the vapor phase embodiment of the present invention, the carbonylation reaction may be carried out by intimately contacting an alcohol with gaseous carbon monoxide in the vapor phase. The temperature preferably is in the range of 50°C to 500°C with the preferred range being 200°C to 400°C. Partial pressures of carbon monoxide of the order of 0.1 psia to 15,000 psia may be employed; however 5 psia to 3,000 psia carbon monoxide partial pressure is generally preferred and a more preferred range is from 10 psia to 700 psia. Higher pressures may be used if desired under appropriate conditions.

In a typical carbonylation process, selective to carboxylic acid, one mole of carbon monoxide reacts with each hydroxyl group (molar basis). More or less carbon monoxide from the aforesaid stoichiometric amount, however,

may be present. Carbon monoxide streams containing inert impurities such as hydrogen, carbon dioxide, methane, nitrogen, noble gases, water and paraffinic hydrocarbons having from 1 to 4 carbon atoms may be employed, if desired, for example, from an available plant gas stream, to good effect; however, in such cases total reactor pressure will have to be increased to maintain a desired carbon monoxide partial pressure. The concentration of carbon monoxide in the feed gas mixture is from 1 vol. % to 99.9 vol. %, a preferred range being from 10 vol. % to 99.9 vol. %.

The reaction rate is dependent upon catalyst concentration and temperature. Concentrations of the noble metal compound, i.e., iridium, platinum, palladium, osmium and ruthenium or the first component of the catalyst system in the liquid phase, between 10^{-6} moles/liter and 10^{-1} moles/liter, are normally employed, with the preferred range being 10^{-4} moles/liter to 10^{-2} moles/liter. Higher concentration even to the extent of 1 mole/liter may, however, be used if desired. Higher temperatures also favor higher reaction rates.

The concentration of excess ligand, such as organo-phosphine, organo-arsine, or organo-stibine above that required to form a stoichiometric coordination compound, if any excess is desired, may vary widely, e.g., from 10^{-6} moles/liter to 10 moles/liter of catalyst solution. However, the preferred concentration range of excess ligand is 10^{-1} moles/liter to 1 mole/liter.

The concentration of the second component or promoter portion of the catalyst system may vary widely over the broad concentration range of 10^{-6} moles/liter to 18 moles/liter, based on halogen atom. In the process of this invention, however, the preferred concentration range of promoter is 10^{-1} moles/liter to 2 moles/liter of catalyst solution.

Concentrations of the noble metal compound or the first component of the supported catalyst system in the vapor phase, between 0.01 wt. % and 10 wt. % are normally employed, with the preferred range being 0.1 wt. % to 5 wt. %. Higher concentrations even to the extent of 20 wt. % may, however, be used if desired.

The concentration of the second component or promoter portion on the support in the vapor phase reaction may vary widely over the broad concentration range of 0.01 wt. % to 30 wt. %, based on halogen atom. In the process of this invention, however, the preferred concentration range of promoter is 1 wt. % to 20 wt. %, relative to the weight of the support.

In the liquid phase embodiment, the active nobel metal, i.e., iridium, platinum, palladium, osmium and ruthenium catalytic component is supplied as a catalyst solution. The solution can also include liquid reactants, products and mixtures thereof which function as solvents or

reaction media. It has been found that the nature of the products obtained in the present carbonylation process can be controlled by the use of various proportions of alcohol, ester and acid as the solvent for such a catalyst solution. A preferred group of solvents is discussed below for use when reacting an alcohol having n carbon atoms where n is a whole number from 1 to 20. This preferred group of solvents is comprised of the said alcohol having n carbon atoms, an acid having $n+1$ carbon atoms, the ester of the said acid and the said alcohol, the diether of the said alcohol, a halide of the said alcohol and mixtures thereof. A still more preferred group of solvents is comprised of the aforesaid alcohol, the acid, and the ester of the said acid and said alcohol.

In carrying out of the above described invention for the production of high proportion of acid, e.g., acetic acid, as the desired product, the charge to the reactor may be pure or may include byproducts which are recycled with the alcohol feed. The purification system may therefore employ a distillation train to recover the acetic acid product by distillation, while the remaining lower boiling components are recycled.

The present process may be operated to produce high proportions of the carboxylic acid or the ester of such carboxylic acids with the feed alcohol to obtain high productivity. Various alcohols may be charged as the alcohol feed, for example, the charging of ethanol yields as primary products propionic acid and ethyl propionate. If it is desired to

increase the proportion of acid, the ester may be recycled to the primary reactor, or may be introduced into another reactor (together with water) for the purpose of forming the acid in a separate zone. When charging a mixture of alcohol and ester, there are particular molar ranges of ratios of alcohol to ester, which are conducive to the formation of certain product distributions, with the broad range of 0.001 to 10,000 moles of alcohol per mole of ester.

Thus the use of an alcohol-ester feed in a ratio of alcohol to ester no more than about 2, preferably 0.001 to 2 (and including a substantially pure ester as the feed) yields a product with a high proportion of acid, e.g., reaching substantially 100% carboxylic acid. Alternatively, the use of a ratio of alcohol to ester greater than about 10, preferably 10 to 10,000 (including a substantially pure alcohol feed) yields a product with a very high proportion of the ester, e.g., reaching substantially 100% ester.

Within the latter alcohol/ester feedstock ratio range of 10 to 10,000 there exist two alternative embodiments of the invention. In the first such embodiment the product consists essentially of 100% ester at alcohol conversion levels up to about 90 mole %; at above about 90% alcohol conversion level the product is substantially completely the acid.

Similarly, ratios of alcohol to ester in the feed, in the range of 2 to 10, permit obtaining various proportions of acid and ester as mixtures in the product.

The above cases are summarized below:

Alcohol/Ester Ratio	Major Product
0.001 to 2	acid
2 to 10	mixed acid and ester
10 to 10,000 a) to about 90% alcohol conv.	ester
b) above about 90% alcohol conv.	acid

An example of the above described embodiment for the production of high proportion of acid, e.g., acetic acid, as the desired product, the charge to the reactor includes a relatively low proportion of the alcohol. Thus in the production of acetic acid, the ratio is no more than 2 moles of methanol per mole of methyl acetate. Consequently, the purification system employs a distillation train to recover the acetic acid product by distillation, while the remaining lower boiling components consisting principally of methyl iodide promoter, unreacted methanol, and methyl acetate are recycled.

In carrying out a second embodiment, described above, for the production of high

proportion of ester, e.g., methyl acetate, as the desired product, the charge to the reactor includes a relatively high proportion of the alcohol, e.g., greater than 10 moles of methanol per mole of methyl acetate.

Consequently, the purification system employs a distillation train to recover the methyl acetate by distillation, while the remaining components consisting principally of the unreacted feedstocks, methyl iodide (or other halide promoters), methanol and water are recycled. The methyl acetate is hydrolyzed for example by contacting with steam, as described herein, thus isolating the acetic acid with the recovery of methyl alcohol, which may be recycled. However, the ester product is often

used, per se for example, as a solvent in chemical processing or for the formulation of coating compositions.

When conducting the liquid phase process in the absence of another compound as solvent having a higher boiling point than acetic acid (discussed below), a portion of the acetic acid product containing the iridium catalyst system (including other inorganic halide compounds as promoter) is recycled to the reactor to return the said catalyst system to the reaction zone.

The reactants which are used in the present processes are essentially aryl- and alkyl-alcohols, and alcohol derivatives such as ethers, esters and organic halides having from 1 to 20 carbon atoms (preferably 1 to 10 carbon atoms), including straight and branched chain components. The second essential component is carbon monoxide. However, the carbon monoxide need not be in a high purity stream such as has been required by prior art processes. Instead, the carbon monoxide may be a low-concentration mixture containing from 1 vol. % to 99.9 vol. % of carbon monoxide, with the remainder of the gas mixture being comprised of gases selected from the group consisting of nitrogen, hydrogen, carbon dioxide, noble gases, water and paraffinic hydrocarbons having from 1 to 4 carbon atoms. Preferred ranges of carbon monoxide are from 30 vol. % to 70 vol. % carbon monoxide with the above gases.

An alternate embodiment of the present invention includes the use of multiphase catalysts comprised of a porous solid carrier upon which a liquid phase catalyst is prepared by addition of a separate high boiling solvent to the preformed active catalyst solution containing both noble metal and halogen promoter components in a more volatile solvent as described above. Subsequently, the active catalyst solution including the high boiling solvent is dispersed upon a carrier. The high boiling point solvent in general has a vapor pressure of 10^{-12} to 10 mm Hg, a preferred range being from 10^{-10} to 1 mm. Examples of solvents include: mineral oil, 1-methyl naphthalene, ethylene glycol, polyphenyl ethers, tetraethylene glycol, diisodecyl phthalate, dioctyl phthalate, bis (2-ethylhexyl)adipate, 1,3-propanediol dioleate, ethylene glycol distearate, polydiethylene glycol adipate, 1,4-butanediol adipate, sucrose acetate isobutyrate, trixylenyl phosphate, perfluorotributylamine, 4-methyl quinoline, high boiling inorganic or organic salts, such as cupric acetate.

When ester is present in the feedstock, it is normally charged with equimolar amounts of water, although more or less water may be used. The reference to the ester in the above ratios, is on the basis that a molar quantity of water is present equivalent to the number of moles of ester present.

It has been found that water generally exerts a beneficial effect on the rate of reaction. However, adding water, with the feed in excess of the equimolar quantity, e.g., an excess of 50% to 300% of such equimolar quantity, already present with ester, as discussed above, promotes the production of the carboxylic acid. On the other hand the production of ester is favoured by operation with smaller quantities of water, e.g., 50% to 100% of the equimolar proportions discussed above.

The above catalyst solutions used in the liquid phase embodiment essentially comprised of: (1) the reactant alcohol-product acid medium, (2) a noble metal, e.g., iridium, platinum, osmium and ruthenium, compound, and (3) a halogen promoter, may be further modified by the addition of a high boiling, inert solvent as a further component. Such an inert solvent must have a boiling point at least 25°C higher (S.T.P.) than the product acid and ester. Inert solvents within the present category include paraffin hydrocarbons of from 10 to 30 carbon atoms, aromatic hydrocarbons of from 12 to 40 carbon atoms, organic acids of from 3 to 20 carbon atoms, and esters composed of the aforesaid acids in combination with the alcohol feedstock undergoing carbonylation, and also orthophosphorus and orthosilicon alkoxy esters in which the alkoxy group has the same number of carbon atoms as the alcohol feedstock undergoing carbonylation, as well as the chlorine, bromine, and iodine containing derivatives of all of the above said solvents. The following list exemplifies such solvents: dodecane, hexadecane, naphthalene, biphenyl, propionic acid, octanoic acid, phthalic acid, benzoic acid, dioctyl phthalate, dimethyl phthalate, ethyl benzoate, didecyl phthalate, dimethyl adipate, triphenyl phosphate, tricressyl phosphate, dibutylphenyl phosphate, tetramethyl orthosilicate, tetrabutyl orthosilicate, chloronaphthalene and chlorinated biphenyls.

The inert solvents, as described, refer to the actual molecular species which are present in the carbonylation reaction mixture. Consequently, modified derivatives may be charged initially, for example, an ester having a number of carbon atoms which is greater or less than the aforesaid ranges by one, two or more carbon atoms. Under reaction conditions in the presence of the feedstock alcohol, such esters undergo ester interchange to equilibrium species which are within the above ranges.

Another embodiment of the process utilizes a high-boiling, inert solvent such as dimethyl phthalate as described above, with the relatively high proportion of the alcohol, together with the active iridium catalyst component and the promoter. In this embodiment, particularly suitable for use with a gas-sparged reactor system, the feed is a liquid such as methyl alcohol with the carbon monoxide introduced in gaseous form. The product stream is then removed as a vapor containing methyl acetate as the principal component. In this embodi-

ment of the invention no liquid is withdrawn, so that a distinct advantage exists because of the elimination of catalyst handling; and consequently a minimization of catalyst losses. The vapor stream leaving the reactor is then condensed; it contains the methyl acetate which is recovered from the liquid condensate by distillation, and a small proportion of acetic acid which is recycled. The methyl acetate is hydrolyzed with water or steam to yield acetic acid as the major product while the methanol resulting from the hydrolysis of the ester is recycled.

Another embodiment of the invention is based upon the use of the carbonylation reaction as described herein for the purification of hydrogen streams containing small percentages, e.g., 0.1 to 10 percent carbon monoxide by volume. Such a gas stream when available in an industrial plant is often desirable as a source of pure hydrogen, but is very difficult to free from carbon monoxide. The present process based upon the use of a noble metal catalyst is readily adaptable to this purification since the carbon monoxide in such a gas mixture readily undergoes reaction with an alcohol, for example, butyl alcohol to yield pentanoic acid. Because of the completeness of reaction, the carbon monoxide is completely removed from the gas mixture while the hydrogen is unreacted, and is easily separated as a pure stream of hydrogen gas. This embodiment of the invention using a noble metal catalyst, i.e., iridium, platinum, palladium, osmium or ruthenium catalyst, represents a major improvement over earlier carbonylation catalysts such as cobalt compounds. The cobalt compounds cannot tolerate the presence of hydrogen since the hydrogen also reacts with the acid and ester products, being catalyzed by the cobalt compounds. Consequently, a major redistribution of products with the production of different, higher acids, alcohols and aldehydes occurs when using cobalt catalysts.

The noble metal catalysts of the present invention are characterized by an unusually high degree of specificity for the carbonylation reaction, e.g., the reaction of alcohols with carbon monoxide to obtain a carboxylic acid. Such control over the various competing reactions to obtain the carboxylic acid in high yield is surprising since other metal catalysts do not show such specificity for this reaction. The iron group metals such as iron, cobalt and nickel differ from the present noble metal catalysts, i.e., iridium, platinum, palladium, osmium and ruthenium, in that the iron group metals simultaneously catalyze the hydrogenation reactions to a very high degree. Consequently, the products obtained include the next higher alcohols as well as aldehydes and carboxylic acids having 2 or more carbon atoms than the starting alcohols. Furthermore, the iron group catalysts, particularly cobalt, require a far higher carbon monoxide partial

pressure to remain stable. When moderate pressures, e.g., less than about 2000 psig carbon monoxide partial pressure are employed, at a temperature of 175°C, the cobalt catalyst is found to plate out or decompose to the free metal which plates on the walls of the reactor and is thus lost as a catalyst.

Another distinction of the noble metal catalysts over the cobalt catalysts is the elimination of undesirable gaseous byproducts, including carbon dioxide and methane which are obtained as a result of the water-gas shift reaction catalyzed by cobalt. Furthermore, significant quantities of the undesirable byproduct, dimethyl ether, are also formed in the presence of the cobalt catalyst system, as shown in Examples 3 and 4 below. This ether compound attains a very high partial pressure at the reaction conditions employed, and necessitates the use of a high total pressure reaction system to maintain the necessary partial pressure of carbon monoxide for reaction to form carboxylic acids, e.g., 2000 psig total pressure for 750 psig carbon monoxide partial pressure, at a reaction temperature of 175°C.

For a better understanding of the process of the present invention specific embodiments of the process are presented below. These examples and illustrations are not to be construed in any way limiting to the scope of the invention.

The drawings, forming a part of the present specification also illustrate certain embodiments of the invention. Figure 1 shows the liquid phase embodiment, while Figure 2 shows the vapor phase embodiment of the invention. Fig. 1 illustrates a process wherein the carbon monoxide is introduced into the reactor 3 through line 1 and is sparged into the liquid solution in the reactor. The gas stream may also contain components which are inert to the reaction such as hydrogen, nitrogen and methane, in addition to the carbon monoxide. A reactor containing 2000 gallons of liquid solution has a concentration of 5×10^{-3} moles/liter of chlorocarbonylbistriphenylphosphine iridium(I) and 0.6 moles/liter iodide, e.g., as methyl iodide. Through this liquid reaction medium a normal gas rate is 85 lb/min carbon monoxide. The reactor operates at 200°C and 500 psig pressure. The liquid feed to the reactor is introduced through line 2. The feed consists of a methanol feed stream used to scrub the effluent gas (line 23), a catalyst recycle stream (line 42), a recycle stream containing principally methyl acetate, unreacted methanol, and methyl iodide (line 45), and a make-up stream to maintain the catalyst and iodide concentration in the reactor (line 43).

The gaseous reactor effluent exits through line 4, is cooled to about 10°C in exchanger 5, and goes to high pressure separator 10. The condensed liquid from separator 10 is removed through line 11; the pressure is let down through valve 12, and the liquid then

goes to low pressure separator 17. The gas leaving the low pressure separator 17, through line 14, consisting principally of carbon monoxide, methyl iodide, methanol, and methyl acetate, mixes with the gas effluent from the high pressure separator (line 13) which is principally carbon monoxide, and enters the methanol scrubber 25 through line 20. In the scrubber, 25, feed methanol introduced through line 22 at a rate of about 80 lb/min is used to remove the small amount of methyl iodide, methyl acetate, and acetic acid from the gas before it leaves the system. The effluent gas exiting through line 21 may either be recycled or if the inert gas content is high, it may be vented or burned. The methanol is removed from scrubber 25 through line 23 and introduced to the reactor as line 23 after being pressured through pump 24.

The liquid effluent from reactor 3 is removed from the reactor through line 6. After pressure let down valve 7, the liquid effluent is introduced into distillation or flash column 30 where the lower boiling compounds are separated from acetic acid and the other less volatile components such as the catalyst system. The lower boiling components consisting principally of methyl acetate, methyl iodide, and unreacted methanol exit through line 31 and mix with the condensed phase from the low pressure separator in line 15 which also contains these low boiling compounds. This mixed stream of line 15 and 31 is compressed by pump 16 and recycled to the reactor as line 45.

The acetic acid and other higher boiling compounds are removed as line 32 from column 30 and enter distillation or flash column 40. In this column acetic acid which may contain water is separated from the other high boiling components, principally comprised of the catalyst. The acetic acid product is withdrawn as line 41 and may be further purified to remove water. The high boiling components exit through line 42 and are brought up to reactor pressure by pump 44. If no component higher boiling than acetic acid, such as a high boiling solvent, is present, then some acetic acid may be recycled through line 42 to return the catalyst to the reactor. A small liquid purge stream may be withdrawn as line 46 to prevent build-up of higher boiling compounds. After removal of impurities from line 46, the catalyst recovered may be added to the make-up stream (line 43).

The process of the present invention may be operated either as a batch or as a continuous process. In batch operation the reactants are charged into the liquid catalyst solution, which is then subjected to the desired temperature and pressure conditions, after which the products are separated from the reaction mixture. In a continuous process which is described above, the catalyst is maintained in liquid state, with the reactants being continuously

supplied to the reaction zone containing the catalyst at the desired temperature and pressure. The products are continuously withdrawn, either in the vapor state or as described above by withdrawing a portion of the catalyst solution also containing unreacted feed, equilibrium components, and the desired product, which are then separated from the catalyst solution to permit recycling of catalyst solution, unreacted feed and also equilibrium components.

In order to show the vapor phase embodiment of the invention Figure 2 illustrates a process wherein the carbon monoxide is introduced by line 101 into the reactor 103 containing the supported noble metal catalyst. The gas stream may also contain components which are inert to the reaction, such as hydrogen, nitrogen and methane, in addition to the carbon monoxide. The reactor 103 contains 1,000 pounds of a catalyst composed of activated carbon of ¼-inch particle size, containing 1% by weight of a noble metal component calculated as elemental noble metal and prepared as discussed above.

The normal gas rate to the reactor 103 is 85 lb/min of carbon monoxide. The reactor operates at 275°C and 100 psig pressure. Line 102 serves to introduce methanol feed plus recycled methyl acetate, unreacted methanol and methyl iodide.

The gaseous reactor effluent exits through line 104 and is used to preheat the feed in exchanger 106. Line 104 is further cooled in exchanger 105 and goes to high pressure separator 10. The condensed liquid from separator 110 is removed through line 111 the pressure is let down through valve 112 and the liquid then goes to low pressure separator 117. The gas leaving the low pressure separator 117, through line 114, consisting principally of carbon monoxide, methyl iodide, methanol and methyl acetate, mixes with the gas effluent from the high pressure separator line 113 which is principally carbon monoxide, and enters the methanol scrubber 125 through line 120. In the scrubber 125, feed methanol introduced through line 122 at a rate of about 80 lb/min is used to remove the small amount of methyl iodide, methyl acetate, acetic acid, and other volatile components from the gas before it leaves the system. The effluent gas exiting through line 121 may either be recycled or, if the inert gas content is high, it may be vented or burned. The feed methanol and recovered components are removed from scrubber 125 through line 123.

The liquid effluent from separator 117 is removed through line 115. This effluent is introduced into distillation column 130 where the lower boiling compounds are separated from acetic acid. The lower boiling components consisting principally of methyl acetate, methyl iodide, unreacted methanol, and other volatile components, exit through line 131 and mix

with the liquid effluent from the scrubber, line 123 to become line 126.

The acetic acid and other higher boiling compounds are removed as line 132 from column 130 and enter distillation column 140. In this column acetic acid which may contain water is separated from the other high boiling components.

The acetic acid product is withdrawn as line 141, and this product may be further purified to remove water. The high boiling components exit through line 142 and mix with line 126 to become the reactor feed, line 102, after being pressured through pump 124 and preheated in exchanger 106. A small liquid purge stream may be withdrawn as line 146 to prevent build-up of high boiling compounds.

The process of the present invention may be operated either as a batch or a continuous process. The present solid catalyst may be employed as a fixed or fluid bed. The reactor may consist of a series of catalyst beds with interstage cooling between the beds or the catalyst may be placed in tubes with a heat exchange medium around the tubes. These tubes containing catalyst may be run in parallel or series. The metal content of the catalyst may be varied through the reactor to provide operating advantages. A bed of the catalyst support, per se, without metal components, may also be used so that the gas stream passes through such a bed in order to pick up any catalyst swept out of the reactor. It is also an embodiment of the invention to use either up-flow or down-flow of the reactants through the reactor, with periodic reversal of the gas stream also being contemplated, to provide operating advantages such as maintaining a clean catalyst bed.

An alternate embodiment includes the use of a reactor in which liquid, gas, and solid phases are present, e.g., trickle or slurry type. The solid consists of a stable supported noble metal component such as zero valent noble metal on a carrier, which is stabilized against dissolution by the liquid phase components condensed under pressure. The gas phase then comprises chiefly carbon monoxide.

In order to illustrate the present invention, specific embodiments of the process are presented below. These examples and illustrations are not to be construed in any way limiting to the scope of the invention. It should be noted that most of the examples are generally held at a low conversion level in order to bring out comparisons of the various factors.

In a preferred method of catalyst preparation, the noble metal component is dispersed upon an inert support and the promoter is subsequently added in the reactor feed.

In another method, the supported catalyst containing both noble metal and halogen promoter components is performed prior to charging the reactor.

EXAMPLE 1

A batch reactor is charged with the following ingredients: 0.554 grams of an iridium compound having the formula $IrCl_3$, 28.8 grams of a promoter consisting of methyl iodide, CH_3I, 196.9 grams of acetic acid as a solvent, and 79 grams of methanol as feedstock.

The reactor is pressurized with carbon monoxide to a total pressure of 1000 psig, corresponding to a carbon monoxide partial pressure of about 800 psig, at the reaction temperature of 175°C. The reaction is carried out at a constant pressure to yield a solution containing the following distribution of products:

$$87.5 \text{ wt } \% \text{ Acetic Acid}$$
$$4.6 \text{ wt } \% \text{ Methyl Iodide}$$
$$8.9 \text{ wt } \% \text{ (Catalyst, etc.)}$$

The selectivity to the formation of the desired acetic acid product is greater than 95% at substantially 100% conversion of methanol. No substantial amounts of byproducts such as aldehydes, dimethyl ether, higher boiling carboxylic acids, methane, or carbon dioxide are formed. The time required for 50% of the methanol to be converted to acetic acid is 82 minutes. The present experiment as well as the other examples, is carried out at a slow rate in order to permit a study of the mechanism of the reaction. However, when the rates are increased to those of a commercial unit, high selectivity and conversions are also obtained.

When this experiment is conducted with the equivalent molar quantity of cobalt chloride instead of iridium chloride as the catalyst, the selectivity and yield of the desired acetic acid product are decreased significantly. It has been found that cobalt catalysts differ radically from iridium catalysts in that the cobalt catalysts also cause hydrogenation reactions such as hydrogenation of the desired carboxylic acid product to aldehydes and alcohols of the same number of carbon atoms. Consequently, the use of cobalt catalysts results in the substantial production of various undesirable byproducts including ethanol, acetaldehyde, and the next higher carbon number carboxylic acid, e.g., propionic acid. Another distinction of the iridium catalysts over the cobalt catalysts is the elimination of undesirable gaseous byproducts, including carbon dioxide and methane which are obtained as a result of the water-gas shift reaction catalyzed by cobalt. Furthermore, significant quantities of the undesirable byproduct, dimethyl ether, are also formed in the presence of the cobalt catalyst system, as shown in Examples 3 and 4 below. This ether compound attains a very high partial pressure at the reaction conditions employed, and necessitates the use of a high total pressure reaction system to maintain the neces-

sary partial pressure of carbon monoxide for reaction to form carboxylic acids, e.g., 2000 psig total pressure for 750 psig carbon monoxide partial pressure, at a reaction temperature of 175°C.

Still another distinction of the iridium catalysts compared to the cobalt catalysts is the fact that lower carbon monoxide partial pressures can be used without encountering metal plating. Thus metal plating or decobalting occurs in Example 4 at 2100 psig carbon monoxide partial pressure, with increasing plating out at lower pressures. In contrast, iridium catalysts do not plate out metal even at 150 psig carbon monoxide partial pressure.

Example 2

A batch reactor is charged with the following ingredients: 1.17 grams of an iridium complex (coordination compound) having the formula $Ir(CO)Cl[P(C_6H_5)_3]_2$, 28.8 grams of a promoter consisting of methyl iodide, CH_3I (ratio of promoter halogen to iridium atoms about 140:1), 196.9 grams of acetic acid as a solvent, and 79 grams of methanol as feedstock.

The reactor is pressurized with carbon monoxide to a total pressure of 1000 psig, corresponding to a carbon monoxide partial pressure of about 800 psig, at the reaction temperature of 175°C. The reaction is carried out at a constant pressure to yield a solution containing the following distribution of products:

93.80 wt % Acetic Acid
2.30 wt % Methyl Iodide
3.90 wt % (Catalyst, etc.)

Selectivity to the formation of the desired carboxylic acid product is greater than 95%, at substantially 100% conversion of methanol. No substantial amounts of byproducts such as aldehydes, dimethyl ether, higher boiling carboxylic acids, methane, or carbon dioxide are formed. The time required for 50% of the methanol to be converted to acetic acid is 200 minutes.

This example demonstrates the effect of the use of an iridium complex as catalyst instead of a simple iridium salt as compared with Example 1.

Example 3

This example demonstrates that cobalt carbonyl is a far less effective catalyst system than the present system of iridium compounds. A batch reactor is charged with the following ingredients: 2.58 grams of cobalt carbonyl, 28.8 grams of a promoter consisting of CH_3I, 165 grams of benzene as solvent, and 79 grams of methanol feedstock. The reactor is initially pressurized with carbon monoxide to a total pressure of 1000 psig (750 psig carbon monoxide partial pressure) at the reaction temperature of 175°C. The reaction is carried out at a constant pressure. More than 50 mole % of

the methanol feedstock is converted to dimethyl ether. Water and a trace amount of methyl acetate are also produced. No acetic acid is obtained.

Example 4

This example demonstrates that cobalt salts are relatively poor catalysts for the production of acetic acid from methanol even when higher pressures of carbon monoxide and higher temperatures are employed. A batch reactor is charged with the following ingredients: 1.57 grams of $Co(C_2H_3O_2)_2.4H_2O$, 3.81 grams of iodine as a promoter, and 237 grams of methanol feedstock. The reactor is initially pressurized with carbon monoxide to a total pressure of 2500 psig (2000 psig carbon monoxide partial pressure) at the reaction temperature of 195°C. Rapid decomposition of the cobalt catalyst to cobalt metal (plating out) occurs. Analysis of the reaction mixture shows that more than 60 mole % of the methanol feedstock is converted to dimethyl ether. A considerable amount of water is also produced, and less than 5 mole % of the methanol feedstock is converted to methyl acetate and acetic acid.

Example 5

This example demonstrates that a compound of iridium in complex combination with triphenylphosphine in an inert solvent and in the presence of additional triphenylphosphine ligand is a reactive catalyst.

A batch reactor is charged with the following ingredients: 1.17 grams of an iridium complex having the formula $[(C_6H_5)_3P]_2IrCOCl$, 19.6 grams of triphenylphosphine ligand, $(C_6H_5)_3P$, 57.5 grams of a promoter consisting of CH_3I, 154 grams of benzene as solvent, and 79 grams of methanol feedstock. The reactor is pressurized with carbon monoxide to a total pressure of 1000 psig (carbon monoxide partial pressure about 750 psig) at the reaction temperature of 175°C. The reaction is carried out at constant pressure to yield a solution containing the following distribution of products (exclusive of solvent):

88.3 wt % Acetic Acid
11.7 wt % Methyl Iodide

Selectivity to formation of the carboxylic acid product is greater than 95% at substantially 100% conversion of methanol. No substantial amounts of byproducts such as aldehydes, dimethyl ether, higher boiling carboxylic acid, methane and carbon dioxide are detected by gas chromatography. The time required for 50% of the methanol to be converted to acetic acid is 113 minutes.

Example 6

A batch reactor is charged with the following ingredients: 1.17 grams of an iridium complex having the formula $IrCOCl[P(C_6H_5)_3]_2$, 18 grams of water, 33.6 grams of a promoter

consisting of potassium iodide, KI (ratio %
I/Ir about 143:1) 178.5 grams of acetic acid
as a solvent, and 79 grams of methanol as
feedstock.

The reactor is pressurized with carbon mon-
oxide to a total pressure of 1000 psig, corres-
ponding to a carbon monoxide partial pressure
of about 800 psig, at the reaction temperature
of 175°C. The reaction is carried out at a
constant pressure to yield a solution containing
the following distribution of products:

88.7 wt % Acetic Acid
3.3 wt % Methyl Iodide
8.0 wt % (Catalyst, etc.)

Selectivity to the formation of the desired
carboxylic acid product is greater than 95%,
at substantially 100% conversion of methanol.
No substantial amounts of byproducts such as
aldehydes, dimethyl ether, higher boiling
carboxylic acids, methane, or carbon dioxide
are formed. The time required for 50% of
the methanol to be converted to acetic acid is
181 minutes.

When potassium bromide, or hydrobromic
acid at equivalent molar concentrations is used,
a similar result is obtained except that the
reaction rate is somewhat slower. This ex-
ample demonstrates the effect of using a
bromide or iodide compound as the source of
promoter halogen.

EXAMPLE 7

A batch reactor is charged with the follow-
ing ingredients: 0.554 grams of an iridium
compound having the formula $IrCl_3$, 57.5
grams of a promoter consisting of methyl
iodide, CH_3I, and 215 grams of a methanol
feedstock containing 10 wt % dimethylether.

The reactor is pressurized with carbon mon-
oxide to a total pressure of 1000 psig, corres-
ponding to a carbon monoxide partial pressure
of about 700 psig, at the reaction temperature
of 175°C. The reaction is carried out at a
constant pressure to yield a solution containing
the following distribution of products:

83.5 wt % Acetic Acid
4.7 wt % Methyl Iodide
12.8 wt % (Catalyst, etc.)

Selectivity to the formation of the desired
carboxylic acid product is greater than 95%,
at substantially 100% conversion of methanol.
No substantial amounts of byproducts such as
aldehydes, dimethyl ether, higher boiling
carboxylic acids, methane, or carbon dioxide
are formed. The time required for 50% of
the methanol to be converted to acetic acid is
69 minutes.

This example demonstrates the effect of an
impure alcohol feedstock having ether in the
alcohol. Thus the commercial alcohol ether
product from a methanol plant is shown as

having no deleterious effect on the reaction as
compared with Examples 1.

EXAMPLE 8

A batch reactor is charged with the
following ingredients: 1.17 grams of an
iridium compound having the formula
$Ir(CO)Cl[P(C_6H_5)_3]_2$, 1.228 grams of addi-
tional triphenylphosphine ligand, 28.8 grams of
promoter consisting of methyl iodide, CH_3I,
25.6 grams of acetic acid, 36.8 grams of water,
49.1 gram of methanol, and 151.2 grams of
methyl acetate, which corresponds to the equi-
librium concentrations of the ester and water
components under the reaction conditions em-
ployed. The reactor is pressurized with carbon
monoxide to a total pressure of 1000 psig,
corresponding to a carbon monoxide partial
pressure of about 750 psig, at the reaction
temperature of 175°C. The reaction
is carried out at a constant volume
until substantially all of the carbon monoxide
is reacted (final reactor pressure about 250
psig, corresponding to substantially zero partial
pressure of carbon monoxide because of the
complete reaction of carbon monoxide).

The reaction product distribution which is
obtained has substantially the same methyl
acetate and water concentrations as initially
charged; however, 58 wt % of the methanol
charged to the reactor is converted to acetic
acid.

No substantial amounts of byproducts such
as aldehydes, dimethyl ether, higher boiling
carboxylic acids, methane or carbon dioxide
are formed. The time required for substan-
tially all of the carbon monoxide to be reacted
with methanol and thus converted to acetic
acid is 120 minutes which corresponds to a
space-time yield (STY) of about 1.5 moles
of product/liter of catalyst solution/hour. The
rate of carbon monoxide conversion is changed
by a factor of less than 2 over this total con-
version range. It is also noted that the rate
parameters of this, and the other examples is
obtained when using a rate sufficiently low
to permit a study of the reaction mechanism.
However, when the rates are increased to those
of a commercial unit, the same high selectivity
and conversions are maintained.

This example demonstrates the process con-
cept of operating a continuous reactor to pro-
duce acetic acid from methanol while main-
taining equilibrium recycle streams of the ester
(methyl acetate) and water, and resulting in a
net conversion of the methanol feedstock to
the desired acetic acid product while main-
taining the said equilibrium conditions.

EXAMPLE 9

A batch reactor is charged with the follow-
ing ingredients: 1.17 grams of an iridium com-
pound having the formula $[(C_6H_5)_3P]_2IrCOCl$,
51 grams of promoter consisting of aqueous
57% hydriodic acid, 179 grams of benzene as

a solvent, and 100 grams of 1,4-butanediol as feedstock. The reactor is pressurized with carbon monoxide to a total pressure of 500 psig, corresponding to a carbon monoxide partial pressure of about 425 psig, at the reaction temperature of 195°C. The reaction is carried out at a constant pressure to yield a solution containing the following distribution of products: 30.7 wt % adipic acid, 69.3 wt % (catalyst, etc.). No substantial amounts of byproducts such as aldehydes, ether, higher boiling carboxylic acids, paraffins or carbon dioxide are formed in adding 1 CO group at each OH group.

EXAMPLE 10

A batch reactor is charged with the following ingredients: 1.17 grams of an iridium compound having the formula $[(C_6H_5)_3P]_2IrCOCl$, 51 grams of a promoter consisting of aqueous 57% hydriodic acid, 150 grams of benzene as a solvent, and 82 grams of heptanol as feedstock. The reactor is pressurized with carbon monoxide to a total pressure of 500 psig, corresponding to a carbon monoxide partial pressure of about 425 psig, at the reaction temperature of 175°C. The reaction is carried out at a constant pressure to yield a solution containing the following distribution of products:

       32.5 wt % Octanoic Acid
       67.5 wt % (Catalyst, etc.)

No substantial amounts of byproducts such as aldehydes, ethers, higher boiling carboxylic acids, paraffins or carbon dioxide are formed.

This example demonstrates the ability of the catalyst system to carbonylate long chain alcohols.

EXAMPLE 11

A batch reactor is charged with the following ingredients: 1.17 grams of an iridium compound having the formula $Ir(CO)Cl[P(C_6H_5)_3]_2$, 28.8 grams of a promoter consisting of methyl iodide, CH_3I, 72 grams of acetic acid as a solvent, and 167 grams of methanol as feedstock, which upon equilibration is equivalent to about the same alcohol/ester feed ratio of 3.4 as in Example 25.

The reactor is pressurized with carbon monoxide to a total pressure of 500 psig, corresponding to a carbon monoxide partial pressure of about 250 psig, at the reaction temperature of 175°C. The reaction is carried out at a constant pressure to yield a solution containing substantially the same product distribution as in Example under similiar reaction conditions.

In accordance with the criteria set forth herein, the product distribution is controlled by the alcohol/ester feed ratio after equilibration even when the initially charged feed contains organic acid and alcohol instead of the preformed ester of the two compounds. Consequently the product distribution is a mixture of acid and ester products in accordance with the alcohol/ester ratio range of 2 to 10.

EXAMPLE 12

A batch reactor is charged with the following ingredients: 1.17 grams of an iridium compound having the formula $Ir(CO)Cl[P(C_6H_5)_3]_2$, 28.8 grams of a promoter consisting of methyl iodide, CH_3I, 30 grams of acetic acid as a solvent, and 210 grams of methanol as feedstock, which is equivalent to an alcohol to ester ratio of about 12 after equilibration.

The reactor is pressurized with carbon monoxide to a total pressure of 500 psig, corresponding to a carbon monoxide partial pressure of about 250 psig, at the reaction temperature of 175°C. The reaction is carried out at a constant pressure to yield a solution having the following composition:

       49.7 wt % Methyl Acetate
       6.3 wt % Acetic Acid
       5.4 wt % Methyl Iodide
       16.5 wt % (Catalyst, etc.)
       22.1 wt % Methanol

Selectivity to the formation of the desired ester product is about 87% at about 67% conversion of methanol. No substantial amounts of byproducts such as aldehydes, dimethyl ether, higher boiling carboxylic acids, methane, and/or carbon dioxide are formed. The time required for the reaction is 185 minutes. The product distribution of a high proportion of ester is in accordance with the criteria set forth herein for an alcohol/ester feed ratio greater than 10, and a methanol conversion of less than 90%.

In this example after equilibration of the initially charged feed mixture, the solution contains about 37 grams of methyl acetate, 196 grams of methanol and only about 0.5 grams of acetic acid. After the reaction, the solution contains about 150 grams of methyl acetate and 19 grams of acetic acid which corresponds to a net production of 122 grams of methyl acetate and 18.4 grams of acetic acid.

EXAMPLE 13

This example illustrates one of the methods of catalyst preparation. A solid supported catalyst containing a palladium component dispersed upon an inert support is prepared in the following manner: 0.53 grams of palladium chloride having the formula $PdCl_2$ is dissolved in 15 ml of water as solvent. The resulting solution is added to 10 g of a support consisting of 12—30 mesh high surface area carbon.

The mixture is dried at 25°C in air for 8 to 16 hours and then vacuum dried at 110°C for 8 to 16 hours. The catalyst is then cal-

cined in nitrogen at 275°C for one hour. The supported catalyst (10 ml) is charged into an 18-inch Pyrex glass vertical reactor 30 mm in diameter. The resulting catalyst bed, 2 cm

5 in depth, is covered with 100 ml of inert packing as a preheater. The process conditions and results are shown in Table 1 along with other data.

The reactor effluent contains the desired

10 carboxylic acid product, including the ester of the acid product and alcohol feedstock, water and unreacted alcohol, carbon monoxide and promoter. The selectivity of alcohol conversion to the desired carboxylic acid and its ester is

15 essentially 100%. Chromatographic analysis indicates that no substantial production of by-products such as aldehydes, higher boiling carboxylic acids and/or alcohols, methane or carbon dioxide occurs.

20 When this experiment is conducted in separate tests with the equivalent molar quantity of cobalt chloride, only trace proportions of acetic acid are obtained (together with some higher acids and esters).

EXAMPLES 14—23

25 The catalysts in Examples 2—10 are prepared by the method described above. The evaluation results for catalysts prepared from a variety of compounds and with various supports are shown in Table 1, with the catalyst

30 compositions and reaction conditions.

Effective carbonylation catalysts may also be prepared from simple noble metal salts dispersed upon inert supports in which the noble metal components are subsequently reduced to

35 the zero valent state with hydrogen or other suitable chemical reducing agents. Significant increase in reactivity occurs at higher temperature and/or pressure, e.g., up to 700 psia and even more, with no ill effect on the sup-

40 ported noble metal catalyst system. By suitable adjustment of operating conditions, productivity of carbonylated product (carboxylic acid plus carboxylate portion of ester) is appreciably enhanced. The catalyst life of the

45 above catalyst is greater than 500 hours.

TABLE 1

Operating Conditions: Feed rate moles/hr. CH$_3$OH 0.27, CH$_3$I 0.02, CO 0.50. Pressure 1 atm.

Example	Metal Salt	Solvent	Support	Final Metal Content (%)	Reaction Temp. (°C)	Major Product Distribution (Wt. %)			
						CH$_3$OH	CH$_3$COOH	CH$_3$COOCH$_3$	CH$_3$I
13	PdCl$_2$.2H$_2$O	H$_2$O	12 × 30 Mesh Carbon (Pittsburgh Act. Carbon)	3.0	210	72.4	0.2	0.9	22.6
14	Pd(NO$_3$)$_2$.XH$_2$O	H$_2$O	Kaiser KA 101 Al$_2$O$_3$	2.8	215	75.6	0.1	0.7	21.5
15	IrCl$_3$	Conc. Aq. HCl	Carbon	3.0	212	74.9	0.1	2.1	21.8
16	Ir(CO)Cl[P(C$_6$H$_5$)$_3$]$_2$	CH$_3$COOH	SiO$_2$ gel (Davison)	2.0	220	75.0	0.1	1.5	22.3
17	RuCl$_3$.3H$_2$O	Conc. Aq. HCl	Carbon	3.0	208	76.3	0.1	0.3	21.6
18	Ru(CO)Cl$_2$[P(C$_6$H$_5$)$_3$]$_3$	CH$_3$COOH	SiO$_2$—Al$_2$O$_3$ (Houdry S65)	3.0	209	72.6	0.2	0.2	20.8
19	OsBr$_3$(CO)[P(C$_6$H$_5$)$_3$]$_2$	C$_6$H$_6$	Carbon	2.5	206	75.2	0.1	0.2	23.5
20	OsCl$_3$	H$_2$O	Harshaw Mg 0601 MgO	2.5	215	74.1	0.1	0.3	23.6
21	H$_2$PtCl$_6$	H$_2$O	Carbon	3.0	201	76.4	0.1	0.2	22.8
22	Pt(CH$_3$)[P(C$_6$H$_5$)$_3$]$_2$I	C$_6$H$_6$	Kaiser KA 101 Al$_2$O$_3$	3.5	203	75.2	0.2	0.5	21.3

EXAMPLE 23

This example illustrates catalyst preparation using another method. A solid supported catalyst containing a noble metal component dispersed upon an inert support is prepared in the following manner: 2.5 grams of iridium chloride trihydrate, having the formula $IrCl_3$, is dissolved in 50 ml of 3 M aqueous acetic acid as solvent. The solution is warmed to 80°C and carbon monoxide is bubbled through the solution until a pale yellow color is obtained. Then the solution is cooled and 5.0 ml of aqueous 57 wt. % HI is added to the solution of iridium compound. Subsequently, the resulting solution containing both the iridium precursor and halogen promoter components is added to 25 g. of a support consisting of 12—30 mesh high surface area carbon. The mixture is vacuum dried at 80°C for 8 to 16 hours. The catalyst is then preheated in nitrogen at 200°C for one hour.

The supported catalyst (10 ml) is charged into an 18-inch Pyrex glass vertical reactor 30 mm in diameter. The resulting catalyst bed, 2 cm in depth, is covered with 100 ml of inert packing as a preheater. The process conditions are similar to those shown in the headnote in Table 1 and the conversion obtained is similar to that found in the iridium run, Example 3.

EXAMPLE 24

A batch reactor is charged with the following ingredients: 11.5 grams of a palladium complex (coordination compound) having the formula $[(n—C_4H_9)_3P]_2PdI_2$, 28.8 grams of a promoter consisting of methyl iodide, CH_3I (ratio of promoter halogen to rhodium atoms about 140:1), 196.9 grams of acetic acid as a solvent, and 79 grams of methanol as feedstock.

The reactor is pressurized with carbon monoxide to a total pressure of 1000 psig, corresponding to a carbon monoxide partial pressure of about 800 psig, at the reaction temperature of 175°C. The reaction is carried out at a constant pressure to yield a solution containing the following distribution of products:

86.92 wt % Acetic Acid
3.46 wt % Methyl Iodide
9.62 wt % (Catalyst, etc.)

Selectivity to the formation of the desired carboxylic acid product is greater than 95% at substantially 100% conversion of methanol. No substantial amounts of byproducts such as aldehydes, dimethyl ether, higher boiling carboxylic acids, methane, or carbon dioxide are formed. The time required for 50% of the methanol to be converted to acetic acid is 11.2 hours. The present experiment as well as the other examples, is carried out at a slow rate in order to permit a study of the mechanism of the reaction. However, when the rates are increased to those of a commercial unit, high selectivity and conversions are also obtained.

When this experiment is conducted with the equivalent molar quantity of cobalt chloride instead of the palladium compound as the catalyst, the selectivity and yield of the desired acetic acid product are decreased significantly. It has been found that cobalt catalysts differ radically from palladium catalysts in that the cobalt catalysts also cause hydrogenation reactions such as hydrogenation of the desired carboxylic acid product to aldehydes and alcohols of the same number of carbon atoms. Consequently, the use of cobalt catalysts results in the substantial production of various undesirable byproducts including ethanol, acetaldehyde, and the next higher carbon number carboxylic acid, e.g., propionic acid. Another distinction of the palladium catalysts over the cobalt catalysts is the elimination of undesirable gaseous byproducts, including carbon dioxide and methane which are obtained as a result of the water-gas shift reaction catalyzed by cobalt. Furthermore, significant quantities of the undesirable byproduct, dimethyl ether, are also formed in the presence of the cobalt catalyst system, as shown in Examples 3 and 4 above. This ether compound attains a very high partial pressure at the reaction conditions employed, and necessitates the use of a high total pressure reaction system to maintain the necessary partial pressure of carbon monoxide for reaction to form carboxylic acids, e.g., 2000 psig total pressure for 750 psig carbon monoxide partial pressure, at a reaction temperature of 175°C.

Still another distinction of the palladium catalysts compared to the cobalt catalysts is the fact that lower carbon monoxide partial pressures can be used without encountering metal plating. Thus metal plating or decobalting occurs in Example 5 at 2100 psig carbon monoxide partial pressure, with increasing plating out at lower pressures. In contrast, palladium catalysts as in Example 4 do not plate out metal even at 300 psig carbon monoxide partial pressure.

EXAMPLE 25

A reactor is charged with the following ingredients: 0.0022 grams of a platinum compound having the formula $Pt(CH_3)[(C_2H_5)_3P]_2I$, 0.067 grams of a promoter consisting of methyl iodide, CH_3I, 0.484 grams of benzene as a solvent, and 0.158 grams of methanol as feedstock.

The reactor is pressurized with carbon monoxide to a total pressure of 300 psig at 25°C, corresponding to a carbon monoxide partial pressure of about 400 psig, at the reaction temperature of 175°C. The reaction is carried out at constant volume for about 16 hours to yield a solution containing the following distribution of products exclusive of solvent:

40.7 wt % Methyl Acetate
2.2 wt % Acetic Acid Acid
7.5 wt % Methyl Iodide
49.6 wt % Unreacted Methanol

No substantial amounts of byproducts such as aldehydes, higher boiling carboxylic acids, methane, and/or carbon dioxide are formed.

This example demonstrates the use of a platinum complex as a catalyst instead of palladium as compared with Example 24.

EXAMPLE 26

A batch reactor is charged with the following ingredients: 3.82 grams of a ruthenium compound having the formula $RuCl_3.3H_2O$. 28.8 grams of a promoter consisting of methyl iodide, CH_3I, 196.9 grams of acetic acid as a solvent, and 79 grams of methanol as feedstock.

The reactor is pressurized with carbon monoxide to a total pressure of 1000 psig, corresponding to a carbon monoxide partial pressure of about 800 psig, at the reaction temperature of 175°C. The reaction is carried out at a constant pressure to yield a solution containing the following distribution of products:

88.7 wt % Acetic Acid
4.2 wt % Methyl Iodide
7.1 wt % (Catalyst, etc.)

No substantial amounts of byproducts such as aldehydes, dimethyl ether, higher boiling carboxylic acids, methane, or carbon dioxide are formed. The time required for 50% of the methanol to be converted to acetic acid is 4.7 hours. The present experiment as well as the other examples, is carried out a a slow rate in order to permit a study of the carbon atoms. Consequently, the use of cobalt catalysts results in the substantial production of various undesirable byproducts including ethanol, acetaldehyde, and the next higher carbon number carboxylic acid, e.g., propionic acid. Another distinction of the ruthenium catalysts over the cobalt catalysts is the elimination of undesirable gaseous byproducts, including carbon dioxide and methane which are obtained as a result of the water-gas shift reaction catalyzed by cobalt. Furthermore, significant quantities of the undesirable byproduct, dimethyl ether, are also formed in the presence of the cobalt catalyst system, as shown in Examples 3 and 4. This ether compound attains a very high partial pressure at the reaction conditions employed, and necessitates the use of a high total pressure reaction system to maintain the necessary partial pressure of carbon monoxide for reaction to form carboxylic acids, e.g., 2000 psig total pressure for 750 psig carbon monoxide partial pressure, at a reaction temperature of 175°C.

Still another distinction of the ruthenium catalysts compared to the cobalt catalysts is the fact that lower carbon monoxide partial pressures can be used without encountering metal plating. Thus metal plating or decobalting occurs in Example 4 at 2100 psig carbon monoxide partial pressure, with increasing plating out at lower pressures. In contrast, ruthenium catalysts as in Example 8 do not plate out metal even at 300 psig carbon monoxide partial pressure.

EXAMPLE 27

A batch reactor is charged with the following ingredients: 0.0037 grams of an osmium compound having the formula $OsBr_2(CO)[P(C_6H_5)_3]_2$, 0.067 grams of a promoter consisting of methyl iodide, CH_3I, 0.484 grams of benzene as a solvent, and 0.158 grams of methanol as feedstock.

The reactor is pressurized with carbon monoxide to a total pressure of 300 psig at 25°C, corresponding to a carbon monoxide partial pressure of about 400 psig, at the reaction temperature of 175°C. The reaction is carried out at constant volume for about 30 hours to yield a solution containing the following distribution of products exclusive of solvent:

39.5 wt % Methyl Acetate
2.3 wt % Acetic Acid
7.9 wt % Methyl Iodide
50.3 wt % Unreacted Methanol

EXAMPLE 28

This example demonstrates that the reaction may be carried out in the presence of hydrogen without the formation of undesirable products such as acetaldehyde, ethanol nor catalyst decomposition. This example is similar to Example 12 except that the reaction is carried out in an atmosphere of 62 vol. % carbon monoxide and 38 vol. % hydrogen corresponding to a synthetic gas mixture at a total pressure of 2000 psig, (1100 psig partial pressure of carbon monoxide). The selectivity to formation of the acetic acid product is greater than 95% at substantially 100% conversion of methanol. No substantial amounts of reduced materials or other byproducts such as aldehydes, dimethyl ether, ethanol, higher boiling carboxylic acids, methane, carbon dioxide, etc. are detected by gas chromatography, thus distinguishing from cobalt catalysts which yield such byproducts as the result of hydrogenation catalyzed by the cobalt. The time required for 50% of the methanol to be converted to acetic acid is 115 minutes.

A similar result is obtained with another synthetic gas mixture, e.g., a 66 vol. % hydrogen, 33 vol. % carbon monoxide, such as is obtained from a commercial unit. The various impurities, e.g., nitrogen, noble gases, hydrogen, carbon dioxide and paraffinic hydrocarbons of 1 to 4 carbon atoms, which are present in such feed gas mixtures, do not adversely affect the present reaction.

EXAMPLE 29

A batch reactor is charged with the following ingredients: 1.17 grams of an iridium compound having the formula [(C₆H₅)₃P]₂IrCOCl, 1.23 grams of additional triphenylphosphine as a ligand, 28.8 grams of a promoter consisting of methyl iodide, 196.9 grams of acetic acid as solvent, and 79 grams of methanol feedstock. The reactor is pressurized with carbon monoxide to a total pressure of 500 psig (about 300 psig carbon monoxide partial pressure) at the reaction temperature of 175°C. The reaction is carried out at a constant pressure to yield a solution containing the following distribution of components, as determined by gas chromatography.

88.5 wt % Acetic Acid
4.2 wt % Methyl Iodide
7.3 wt % (Catalyst, etc.)

No methanol or methyl acetate is detected. Selectivity to formation of the carboxylic acid product is greater than 95% at substantially 100% methanol conversion. No undesirable byproducts such as aldehydes, dimethyl ether, higher boiling carboxylic acids, methane, carbon dioxide, etc. are detected by gas chromatography. The time required for 50% of the methanol to be converted to acetic acid is 200 minutes.

This example demonstrates that the use of a carbon monoxide partial pressure as low as 300 psig gives similar results to use of the higher partial pressure of carbon monoxide. The results show that the use of high pressures (e.g., 5000—15,000 psig) such as are required with cobalt catalysts are not necessary when using the iridium catalysts of the present invention.

The molar ratio of alcohol to ester in the feedstock in the present Example is about 0.001 (which corresponds to a substantially pure methyl acetate feedstock) in the presence of acetic acid as solvent. The acetic acid solvent and methanol feedstock readily esterify. In accordance with the criteria set forth above, the ratio of alcohol to ester is the controlling factor in product distribution. Consequently the product of this reaction is substantially completely acetic acid.

EXAMPLE 30

This example demonstrates the effect of the rate of reaction as a function of the concentration of the iodine containing promoter. This example is similar to Example 5 except that only 28.8 grams of methyl iodide promoter is added. The selectivity to formation of carboxylic acid product is greater than 95% at substantially 100% conversion of methanol. No substantial amounts of byproducts such as aldehydes, dimethyl, etc. are detected by gas chromatography. The time required for 50% of the methanol to be converted to acetic acid is 245 minutes as compared with 113 minutes in Example 5 when twice as much promoter is used.

The ratio of alcohol to ester in the feedstock in this example is about 10,000 (which corresponds to a substantially pure methanol feedstock) even in the presence of benzene as an inert solvent. Also the conversion level of the methanol feedstock is greater than 90%. In accordance with criteria set forth above the product of this reaction is substantially completely acetic acid.

EXAMPLE 31

A batch reactor is charged with the following ingredients: 1.32 grams of an iridium compound having the formula, Ir(CO)Cl[As(C₆H₅)₃]₂, 28.8 grams of a promoter consisting of methyl iodide, CH₃I, 196.9 grams of acetic acid as a solvent, and 79 grams of methanol as feedstock.

The reactor is pressurized with carbon monoxide to a total pressure of 1000 psig, corresponding to a carbon monoxide partial pressure of about 800 psig, at the reaction temperature of 175°C. The reaction is carried out at a constant pressure to yield a solution containing the following distribution of products:

85.4 wt % Acetic Acid
4.7 wt % Methyl Iodide
10.9 wt % (Catalyst, etc.)

Selectivity to the formation of the desired carboxylic acid product is greater than 95% at substantially 100% conversion of methanol. No substantial amounts of byproducts such as aldehydes, dimethyl ether, higher boiling carboxylic acids, methane, or carbon dioxide are formed. The time required for 50% of the methanol to be converted to acetic acid is 216 minutes.

This example demonstrates the effect of triphenylarsine as a ligand.

EXAMPLE 32

A batch reactor is charged with the following ingredients: 1.17 grams of an iridium compound having the formula [(C₆H₅)₃P]₂Ir(CO)Cl, 57.6 grams of a promoter consisting of methyl iodide, CH₃I, 196.9 grams of acetic acid as a solvent, and 79 grams of methanol as feedstock.

The reactor is pressurized with carbon monoxide to a total pressure of 400 psig, corresponding to a carbon monoxide partial pressure of about 130 psig, at the reaction temperature of 200°C. The reaction is carried out at a constant pressure to yield a solution containing the following distribution of products:

87.9 wt % Acetic Acid
7.9 wt % Methyl Iodide
4.2 wt % (Catalyst, etc.)

Selectivity to the formation of the desired carboxylic acid product is greater than 95% at substantially 100% conversion of methanol. No substantial amounts of byproducts such as aldehydes, dimethyl ether, higher boiling carboxylic acids, methane, or carbon dioxide are formed. The time required for 50% of the methanol to be converted to acetic acid is 52 minutes.

The present work Example demonstrates that high reactivity is obtained even at low carbon monoxide partial pressure, and extending down to about 1 psig partial pressure.

EXAMPLE 33

A batch reactor is charged with the following ingredients: 1.17 grams of an iridium compound having the formula $Ir(CO)Cl[P(C_6H_5)_3]_2$, 28.8 grams of a promoter consisting of methyl iodide, CH_3I, 178.5 grams of acetic acid as a solvent, and 79 grams of methanol as feedstock and 18 grams of water.

The reactor is pressurized with carbon monoxide to a total pressure of 1000 psig, corresponding to a carbon monoxide partial pressure of about 800 psig, at the reaction temperature of 175°C. The reaction is carried out at a constant pressure to yield a solution containing the following distribution of products:

> 90.1 wt % Acetic Acid
> 3.4 wt % Methyl Iodide
> 7.5 wt % (Catalyst, etc.)

Selectivity to the formation of the desired carboxylic acid product is greater than 95% at substantially 100% conversion of methanol. No substantial amounts of byproducts such as aldehydes, dimethyl ether, higher boiling carboxylic acids, methane, or carbon dioxide are formed. The time required for 50% of the methanol to be converted to acetic acid is 153 minutes.

This example demonstrates the beneficial effect upon the reaction rate of adding water to the reaction medium.

EXAMPLE 34

A batch reactor is charge with the following ingredients: 0.554 grams of an iridium compound having the formula $IrCl_3$, 51 grams of a promoter consisting of aqueous 57% hydriodic acid, 150 grams of benzene as a solvent, and 100 grams of phenol as feedstock.

The reactor is pressurized with carbon monoxide to a total pressure of 500 psig, corresponding to a carbon monoxide partial pressure of about 425 psig, at the reaction temperature of 195°C. The reaction is carried out at a constant pressure to yield a solution having the following distribution of products: 34.1 wt % benzoic acid, 65.9 wt % (catalyst, etc.). This example demonstrates the ability of the catalyst system to carbonylate phenols.

EXAMPLE 35

This example demonstrates that compounds of iridium(O) in addition to the compounds of iridium(I) and iridium(III) described above, may be charged as catalysts for the carbonylation of alcohols and alcohol derivatives.

A batch reactor is charged with the following ingredients: 0.414 grams of an iridium(O) compound with the formula $Ir_4(CO)_{12}$, 28.8 grams of a promoter consisting of methyl iodide, CH_3I, 196.9 grams of acetic acid as solvent, and 79 grams of methanol as feedstock.

The reactor is pressurized with carbon monoxide to a total pressure of 1000 psig, corresponding to a carbon monoxide partial pressure of about 800 psig, at the reaction temperature of 175°C. The reaction is carried out at a constant pressure to yield a solution containing the following distribution of products:

> 87.5 wt % Acetic Acid
> 4.1 wt % Methyl Iodide
> 8.4 wt % (Catalyst, etc.)

The selectivity to the formation of the desired acetic acid product is greater than 95%, at substantially 100% conversion of methanol. No substantial amounts of byproducts such as aldehydes, dimethyl ether, higher boiling carboxylic acids, methane, or carbon dioxide are formed. The time required for 50% of the methanol to be converted to acetic acid is 95 minutes.

The word PYREX used in the specification is a Registered Trade Mark.

Catalysts of use in this invention are described and claimed in Application No. 59546/70 Serial No. 1234642 divided herefrom.

WHAT WE CLAIM IS:—

1. A process for the treatment of a reactant which is an alkyl compound having n carbon atoms, where n is a number from 1 to 20, or an aryl compound having n carbon atoms, where n is a whole number from 6 to 20, the said reactant being an alcohol, halide, ester, ether or phenol, to obtain a mixture comprising an organic acid having n + 1 carbon atoms, or an ester of the alcohol having n carbon atoms with the said acid, the said process comprising reacting the said reactant at a temperature of at least 50°C, with carbon monoxide in the presence as catalyst, of a noble metal component selected from iridium, platinum, palladium, osmium and ruthenium and their compounds, and a promoter substance which is a halogen or halogen compound.

2. A process according to claim 1 wherein the promoter substance is selected from bromine, iodine, and compounds of bromine and of iodine.

3. A process according to claim 1 or 2,

wherein the reaction is effected in the presence of a solution containing the noble metal component.

4. A process according to claim 3 wherein the acid solution also contains water.

5. A process according to claim 3 wherein the said solution contains an inert solvent having a boiling point which is at least 25°C (S.T.P.) higher than the said acid and ester obtained.

6. A process according to any of claims 1—5 wherein the partial pressure of carbon monoxide is from 1 psig to 15,000 psig.

7. A process according to claim 6 wherein the partial pressure of carbon monoxide is from 5 psig to 3,000 psig.

8. A process according to claim 6 wherein the partial pressure of carbon monoxide is from 10 psig to 1,000 psig.

9. A process according to any of the preceding claims for the manufacture of acetic acid and/or methyl acetate, wherein the said reactant is methanol, methyl acetate, dimethyl ether or methyl iodide.

10. A process according to claim 9 wherein the reaction is effected at a temperature of from 50°C. to 300°C.

11. A process according to claim 9 or 10 in which the catalyst is a solution of a said noble metal component which also contains acetic acid.

12. A process according to claim 1 or 2, wherein the reaction is in the presence of a supported catalyst comprising a said noble metal component supported upon a carrier.

13. A process according to claim 12 wherein the reaction is effected in vapour phase at a temperature of from 50°C to 500°C.

14. A process according to claim 13 for the manufacture, with reactants and products in the vapour phase, of acetic acid and/or methyl acetate, wherein the reactant is methanol, methyl acetate, dimethyl ether or methyl iodide.

15. A process according to claim 14 in which the reactant is methanol and the feedstock also contains water.

16. A process according to claim 15 in which the said feedstock also contains methyl acetate.

17. A process according to any of claims 12—16 wherein the noble metal component is a noble metal oxide.

18. A process according to any of claims 13—18 in which the partial pressure of carbon monoxide is from 0.1 psia to 15,000 psia.

19. A process according to claim 18 in which the partial pressure of carbon monoxide is from 5 psia to 3,000 psia.

20. A process according to claim 18 in which the partial pressure of carbon monoxide is from 10 psia to 700 psia.

21. A process according to any of claims 12—20 in which the said carrier is carbon.

22. A process according to any of claims

1—21 in which the said promoter is iodine or a compound thereof.

23. A process according to claim 22 in which the said promoter is an alkyl iodide in which the said alkyl radical has 1—20 carbon atoms.

24. A process according to any of claims 1—23 for the production of a high proportion of acid relative to ester, which comprises conducting the process, with the ratio of alcohol to ester being from 0.001 to 2.0.

25. A process according to any of claims 1—23 for the production of a high proportion of ester relative to acid, which comprises conducting the process with the proportion of the alcohol relative to the ester being from 10 to 10,000.

26. A process according to any of claims 1—23 comprising conducting the process with the ratio of the alcohol to the ester being from 0.001 to 10,000.

27. A process according to any of claims 1—26 in which the carbon monoxide is supplied as a gas mixture containing from 1 vol. % carbon monoxide to 99.9 vol. % carbon monoxide, and with the remainder of said gas mixture being selected from the group consisting of nitrogen, noble gases, hydrogen, carbon dioxide, water and paraffinic hydrocarbons having from 1 to 4 carbon atoms.

28. A process according to any of claims 1—16 in which the noble metal component is a noble metal halide.

29. A process according to any of claims 1—16 in which the noble metal component is noble metal carbonyl halide.

30. A process according to any of claims 1—16 in which the noble metal component is a noble metal chloride.

31. A process according to any of claims 1—16 in which the noble metal component is an aryl phosphine complex of the noble metal.

32. A process according to any of claims 1—16 in which the noble metal component contains carbon monoxide and at least one halogen ligand selected from chlorine, bromine and iodine; and at least two ligands selected from phosphorus, arsenic, and antimony derivatives having aryl radicals from 6 to 18 carbon atoms.

33. A process according to any of claims 1—16 in which the noble metal component contains at least one halogen ligand selected from chlorine, bromine and iodine; and at least two ligands selected from phosphorus, arsenic and antimony derivatives having alkyl radicals of from 1 to 18 carbon atoms.

34. A process according to any of claims 1—16 in which the noble metal component contains at least two ligands selected from chlorine, bromine and iodine; alkyl radicals of from 1 to 18 carbon atoms, and aryl radicals of from 6 to 18 carbon atoms; and at least one ligand selected from phosphorus, arsenic and antimony derivatives having radicals selected

from alkyl radicals of from 1 to 18 carbon atoms, and aryl radicals having from 6 to 18 carbon atoms.

35. A process according to claim 1 in which the noble metal component is an iridium halide, an iridium carbonyl halide or an aryl phosphine complex of iridium.

36. A process according to claim 35 in which the noble metal component is iridium trichloride.

37. A process according to claim 1 in which the noble metal component is di-iodobis (tri-butylphosphine) palladium (II).

38. A process according to claim 1 in which the noble metal component is iodomethanebis (triethylphosphine) platinum.

39. A process according to claim 1 in which the noble metal component is a ruthenium halide, a ruthenium carbonyl halide or an aryl phosphine complex of ruthenium.

40. A process according to claim 39 in which the noble metal component is ruthenium trichloride.

41. A process according to claim 1, in which the noble metal component is

$$OsBr_2(CO)[P(C_6H_5)_3].$$
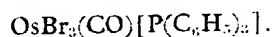
42. A process according to claim 1 substantially as hereinbefore described with reference to any one of the foregoing specific Examples.

43. A process for the transformation of an alcohol having n carbon atoms to a mixture comprised of an acid having $n+1$ carbon atoms, the ester of the said alcohol with the said acid, and mixtures thereof, which comprises contacting the said alcohol with carbon monoxide in the presence of a solution containing a metal compound selected from the group consisting of platinum and palladium compounds, and a promoter substance selected from the group consisting of bromine, iodine, and compounds of said halogens at a temperature of from 50°C to 300°C.

44. A process for the transformation of an alcohol having n carbon atoms to a mixture comprised of an acid having $n+1$ carbon atoms, the ester of the said alcohol with the said acid, and mixtures thereof, which comprises contacting the said alcohol with carbon monoxide in the presence of a solution containing an iridium compound, and a promoter substance selected from the group consisting of bromine, iodine, and compounds of said halogens at a temperature of from 50°C to 300°C.

45. A process for the transformation of an alcohol having n carbon atoms to a mixture comprised of an acid having $n+1$ carbon atoms, the ester of the said alcohol with the said acid, and mixtures thereof, which comprises contacting the said alcohol with carbon monoxide in the presence of a solution containing a metal compound selected from the group consisting of osmium and ruthenium compounds and a promoter substance selected from the group consisting of bromine, iodine, and compounds of said halogens at a temperature of from 50°C to 300°C.

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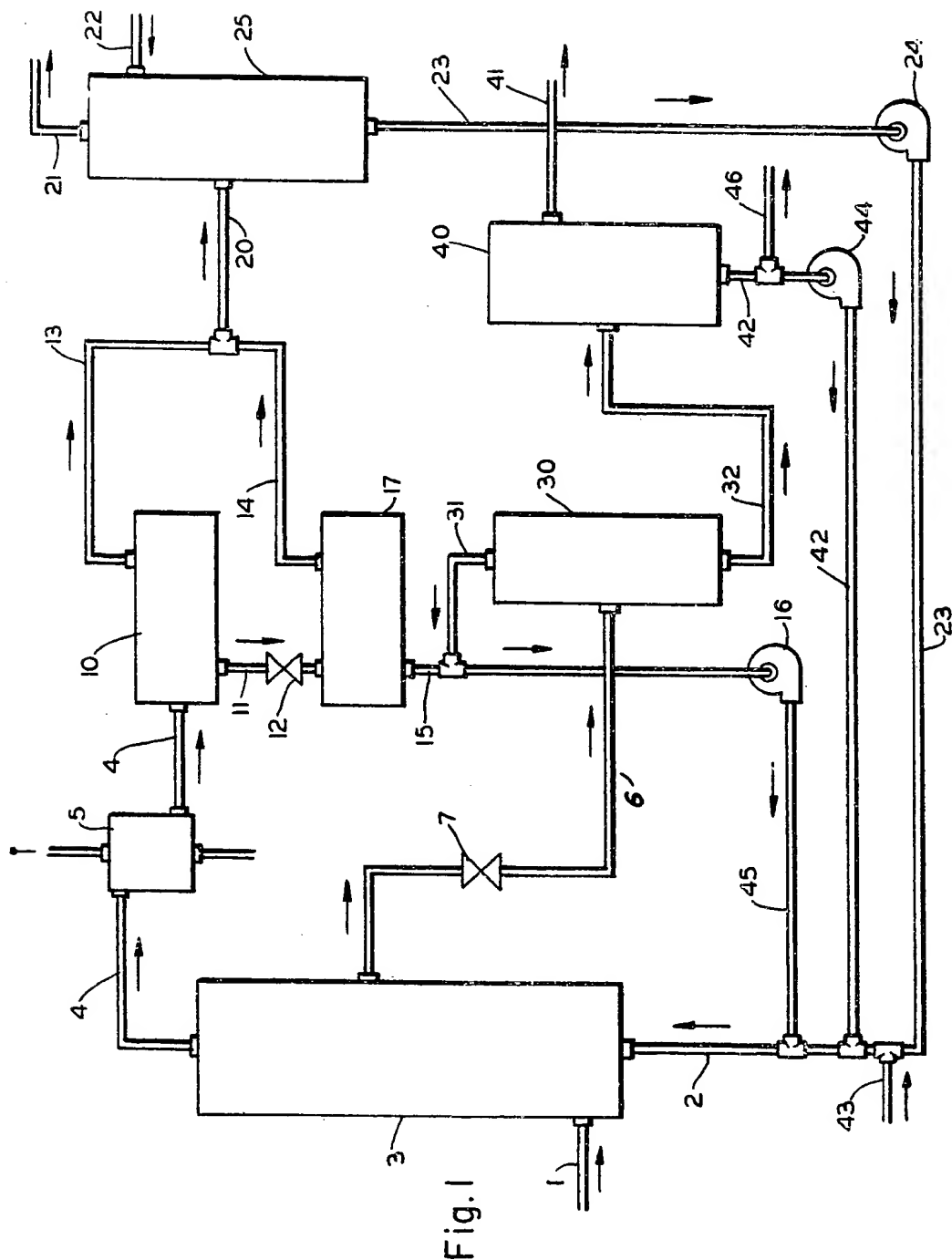
1,234,641   COMPLETE SPECIFICATION

2 SHEETS   This drawing is a reproduction of
the Original on a reduced scale.
SHEET 1

Fig.1

Fig. 2